



Mary-Ann Warmerdam  
Director

Arnold Schwarzenegger  
Governor

**DEPARTMENT OF PESTICIDE REGULATION  
PESTICIDE REGISTRATION AND EVALUATION COMMITTEE  
Meeting Minutes – July 20, 2007 (amended)**

Committee Members/Alternates in Attendance:

Martha Harnly, Department of Public Health (DPH-EHIB)  
Barry Wilson, University of California Department of Environmental Toxicology (UCD)  
Syed Ali, State Water Resources Control Board (SWRCB)  
Matt Hengel, University of California IR-4 Program  
Anna Fan, Office of Environmental Health Hazard Assessment (OEHHA)  
Stella Borucki, Department of Fish and Game (DFG)  
Lynn Baker, Air Resources Board (ARB)  
Dave Whitmer, California Agriculture Commissioners and Sealers Association (CACASA)  
Bryan Eya, Department of Toxic Substances Control (DTSC)  
Brian Larimore, Integrated Waste Management Board (IWMB)  
Barbara Todd, Department of Food and Agriculture (CDFA)  
Tobi Jones, Department of Pesticide Regulation (DPR)

Visitors in Attendance:

Rachel Kubiak, DPR  
Denise Webster, DPR  
Kean Goh, DPR  
Eileen Mahoney, DPR  
Terry Stark, California Association of Pest Control Advisors (CAPCA)  
Bob Ehn, Makhteshim-Agan  
Roger Isom, Cotton Ginner Association  
Nan Singhasemanon, DPR  
John Sanders, DPR  
Sheryl Beauvais DPR  
Shifang Fan, DPR  
Marilyn Silva, DPR  
Joyce Gee, DPR  
Joseph Frank, DPR  
Wes Carr, DPR  
Derek Gammon, DPR  
Jeanne Martin, DPR  
Fred Bundock, DPR  
Marshall Lee, DPR  
Artie Lawyer, Technical Sciences Group (TSG)  
Jim Wells, Environmental Solutions  
Darren Van Steenwick, Clark Pest Control  
Greg Hyatt, Inside Washington Publishers



1. Introductions and Committee Business - Tobi Jones, Chairperson, DPR
  - a. About 36 people attended the meeting.
  - b. There were no corrections to the minutes of the previous meeting held on May 18, 2007.
2. Toxic Air Contaminant Workshop (Endosulfan) – Shifang Fan, Environmental Monitoring Branch; Sheryl Beauvais, Worker Health and Safety Branch; and Marilyn Silva, Medical Toxicology Branch

Doctors Fan, Beauvais, and Silva discussed the draft risk characterization document for endosulfan as it pertains to DPR proposing to list endosulfan as a toxic air containment.

#### **Environmental fate and use**

Dr. Fan presented information on the environmental fate of endosulfan under three broad headings: physical and chemical properties, application and use in California, and its fate in the environment. Endosulfan belongs to the organochlorine group and sub-group of chlorinated cyclodiene, but with only one double bond. Its molecular structure has two stereochemical isomers,  $\alpha$ - and  $\beta$ -endosulfan. For physical/chemical properties, endosulfan is relatively poorly soluble in water, but readily soluble in common organic solvents.  $\alpha$ -endosulfan has higher vapor pressure ( $3.0 \times 10^{-6}$  for  $\alpha$ - vs.  $7.2 \times 10^{-7}$  mm Hg at 25 °C for  $\beta$ -endosulfan), so it is more volatile.  $\beta$ -endosulfan has higher adsorption coefficient ( $1.36 \times 10^4$  for  $\beta$ - vs.  $1.06 \times 10^4$  cm<sup>3</sup>/g for  $\alpha$ -endosulfan), therefore it has more affinity to be adsorbed onto soil surfaces. Henry's Law Constants are estimated of  $4.9 \times 10^{-6}$  and  $1.2 \times 10^{-6}$  atm-m<sup>3</sup>-mol<sup>-1</sup> for  $\alpha$ - and  $\beta$ -endosulfan, respectively. Endosulfan is a broad-spectrum, non-systemic insecticide and acaricide with contact and stomach action. It is used to control sucking, chewing, and boring insects on a wide variety of crops. Currently, there are six registered endosulfan products in California. Formulations include emulsifiable concentrate, wettable powder, and technical grade endosulfan. All labels bear signal word "DANGER-POISON". Endosulfan is a restricted pesticide in California. In recent ten years, annual endosulfan use decreased from more than 200, 000 pounds in 1996 and 1997 (the two years when ambient and application monitoring studies were conducted) to around 83, 000 pounds in 2005. The decreased use in 2005 was mainly due to reduction of cotton crop in the San Joaquin Valley. The top use counties are Fresno, Kings, Imperial, Kern, Tulare, and the peak use months were June to September. Endosulfan was mainly used on cotton, alfalfa, lettuce, tomato, and melons in California.

The physicochemical properties of endosulfan determine its fate in environment. Its overall moderately volatile and adsorptive properties enable it to be transported to multiple media, persist in the environment for an extended period and redistribute to off-target areas. Therefore, endosulfan has been detected in areas where it was never used. The main transportation routes are volatilization, spray drift, and runoff. The main degradation

processes are hydrolysis and oxidation with the main degradates of endosulfan diol and endosulfan sulfate. In the atmosphere, volatilization and vapor transportation are the main processes for endosulfan entering to and moving in the atmosphere. Spray drift from applications resulted in endosulfan unintentionally moving to off-target areas. Importance of dust dispersion and transportation depends on regional weather, geography and topography conditions, and human activities. Wintertime dormant spray may result in wet atmospheric endosulfan in rain and snow. Endosulfan is not susceptible to atmospheric degradation. Half-life was estimated of  $1.4 \pm 0.2$  years for  $\alpha$ -endosulfan. Endosulfan concentration in air is dependent on the distance from the application site. For short-range transportation, seasonal variations typically mirror the agricultural application period. For regional range transportation to the Great Lake area, a distinct annual cycle with summertime averages of peak concentration for  $\alpha$ -endosulfan one or two orders of magnitude higher than that in winter. For long distance transportation to the Arctic, average air concentrations ranged  $1-10 \text{ pg/m}^3$ . Air Resource Board measured ambient and application site air concentrations in California. Committee members were interested in reasons for the decline in use.

### **Exposure Estimates**

Dr. Sheryl Beauvais presented DPR's estimates for exposures of the public to endosulfan in ambient air and exposures of bystanders during applications, and explained how they were calculated based on air monitoring conducted in 1996 and 1997. Ambient air exposure estimates were estimated from total ( $\alpha$ -endosulfan and  $\beta$ -endosulfan) endosulfan concentrations at the 1996 ambient monitoring site having the highest concentrations. Seasonal average daily dosage (seasonal ADD) for ambient air exposures in Fresno County was  $0.000019 \text{ mg/kg/day}$  for infants and  $0.000009 \text{ mg/kg/day}$  for adults. Annual ADD ambient air estimates were  $0.000011 \text{ mg/kg/day}$  for infants and  $0.000005 \text{ mg/kg/day}$  for adults.

Bystander exposure estimates were based on air monitoring done 6 - 18 m from the edge of a San Joaquin County apple orchard during an application in 1997. Concentrations used to estimate short-term absorbed daily dosage (STADD) were adjusted to reflect that the application rate used in this study was below the maximum allowed rate. STADD for bystanders is  $0.00124 \text{ mg/kg/day}$  for infants and  $0.00059 \text{ mg/kg/day}$  for adults. Seasonal ADD estimates for bystander exposures to endosulfan were  $0.00046 \text{ mg/kg/day}$  for infants and  $0.00022 \text{ mg/kg/day}$  for adults. Annual ADD estimates for bystanders were  $0.000038 \text{ mg/kg/day}$  for infants and  $0.000018 \text{ mg/kg/day}$  for adults.

The above exposure estimates are anticipated to increase due to results of quality assurance sampling that was conducted during the studies. Quality assurance included air sampling tubes spiked with known amounts of  $\alpha$ -endosulfan and  $\beta$ -endosulfan; some of these tubes (called "field spikes") were attached to sampling pumps during sample collection. Air monitoring results will be corrected for recoveries of field spikes. The corrected results and exposure estimates were presented.

Committee members requested additional information on the field spikes and how airborne concentrations of endosulfan might be anticipated to vary with air and ground applications. DPR will include responses to these questions in the exposure assessment.

### **Human Health Assessment**

Dr. Marilyn Silva discussed the toxicity of endosulfan and the calculation of risks. The primary mechanism of toxicity with exposure to endosulfan is blockage of or otherwise interference with the (-amino butyric acid (GABA) receptor-binding/chloride ion channel complex in the central nervous system. The complex is initiated under normal circumstances when GABA binds its receptor. Chloride ions then flow across the cell membrane to neutralize the cell interior and terminate fast signaling, or cell excitation. When endosulfan blocks the

Cl<sup>-</sup> channel or otherwise interferes with the binding complex, the nerve stimulation remains; manifesting in neurotoxicity such as convulsions, tremors. In most cases, neurotoxicity was the most sensitive endpoint with acute, subchronic and chronic exposure to endosulfan. The No Observed Effect Level (NOEL) selected for evaluating acute exposure to endosulfan (0.194 mg/kg/day) was based on a subchronic rat inhalation study where rats were treated 21 times over 29 days (6 hours/day, 5 days/week), followed by a 29-day recovery period. This was the best selection for the NOEL since there were no acceptable acute inhalation studies and the use of the subchronic study provided a conservative estimate for acute NOEL (acute NOELs are usually higher than subchronic or chronic NOELs). The same study was used for the critical subchronic NOEL since it was an acceptable, route specific study. For the critical NOEL, the same study was used with an additional 10x uncertainty factor to give a NOEL of 0.0194 mg/kg/day.

With regard to other factors, there was no evidence of oncogenicity observed from *in vivo* studies or *in vitro* genotoxicity studies. While endocrine effects occurred in male rats, they were observed only at neurotoxic doses.

The risk for non-carcinogenic health effects in humans is expressed as the margin of exposure (MOE) that is a ratio of the NOEL from the animal studies to the human exposure dosage. Generally, an MOE greater than 100 is desirable assuming humans are 10 times more sensitive than animals and there is a 10-fold variation in the sensitivity of the human population. The criteria for listing a pesticide as a toxic air contaminant (TAC) is achieved when the MOE is less than 1,000. Using the human exposure dosages estimated from the ambient air and bystander monitoring that was conducted in San Joaquin Elementary School (ambient air; San Joaquin County, 1996) and East Station (bystanders; San Joaquin County, 1997), MOEs were calculated. The findings showed that all MOEs for bystander air were less than 1000 and that ambient air annual MOEs for infants were less than 1000, thereby showing that endosulfan is a potential candidate for listing as a TAC. MOEs that were greater than 1000 included ambient air seasonal (infant & adult) and annual (adult). Committee

members provided comments on the use of single studies for establishing the critical NOELs, and endocrine effects. Dr. Jones announced that the public comment period is open until August 17, 2007, but may be extended.

3. Report on the Investigation of Antifouling paints – Nan Singhasemanon, Environmental Monitoring Branch

In the late 1980's, recreational and commercial boater transitioned from the use of tri-butyl tin to copper as the preferred type of boat hull antifouling paint (AFP). This occurred as a result of regulations developed in response to the toxic effects of tri-butyl tin to aquatic life. A decade later, a recreational boat basin in San Diego Bay known as the Shelter Island Yacht Basin (SIYB) appeared on the Clean Water Act impaired water bodies (303d) list due to beneficial use impairment from copper. The San Diego Regional Water Quality Control Board subsequently began development of a Total Maximum Daily Load (TMDL) for SIYB. Since AFPs are registered as pesticides, DPR assisted on TMDL development.

The SIYB TMDL triggered a number of events including an international AFP workshop in 2000 and the formation of the San Diego Advisory Committee for Environmentally Superior Antifouling Paints. Soon after, DPR convened an interagency workshop to survey the availability of data indicative of copper AFP pollution in California.

To more fully assess the extent of copper AFP pollution, DPR established the Copper AFP Sub-Workgroup (CSG) in March 2004 under the Non-Point Source Interagency Coordinating Committee's Marina and Recreational Boating Workgroup. This forum, which is well-attended by a number of interested stakeholder groups, meets bi-monthly to assess the geographical distribution and magnitude of copper pollution from AFP use in California. Moreover, the CSG tracked and evaluated crucial AFP topics such as U.S. EPA re-registration, changes to the federal water quality criteria, federal attempts at regulating military and non-military vessel discharges, feasibility of alternatives, aquatic invasive species concerns, and AFP-related TMDLs. Nonetheless, the activity of identifying and generating monitoring data remained the focal point of the workgroup.

The CSG coordinated and tracked many monitoring studies. The most significant of these was a study to assess occurrences and concentrations of AFP pollution indicators (e.g., copper, zinc, Irgarol, toxicity) in California marina areas. DPR collected water from 23 marinas for a total of 69 sampling events in the summer of 2006. Some notable observations from the preliminary results include:

- Copper levels (particularly in many salt water marinas) were frequently above enforceable California Toxics Rule (CTR) standards
- Zinc levels never exceeded CTR standards

- Copper levels and toxicity results were comparable to the results of other recent marina studies along the Southern California coast;
- Copper levels in marinas were almost always higher than local reference levels suggesting that marinas are “hot spots” and boat AFPs are the likely source
- Irgarol and its metabolites were ubiquitous in marina waters often at levels that could affect algal and aquatic plant communities
- Copper levels at Marina del Rey were very high and toxicity was observed there

DPR will be evaluating AFP information and data (including those from the statewide study) over the next few months. DPR plans to formulate its regulatory and/or mitigation decisions in September 2007.

4. Agenda Items for Next Meeting- Tobi Jones, DPR

The next meeting will be held on Friday, September 21, 2007, in the Sierra Room on the second floor of the Cal/EPA building, located at 1001 I Street, Sacramento, California.

5. Closing Comments - Tobi Jones, DPR

The meeting was adjourned.